PA NT COOPERATION TREAT''

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 16 February 2001 (16.02.01)	
International application No. PCT/EP00/04997	**Applicant's or agent's file reference** TS 0858 PCT
International filing date (day/month/year) 30 May 2000 (30.05.00)	**Priority date** (day/month/year) 03 June 1999 (03.06.99)
Applicant GEUS, Eduard, Rudolf et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

02 January 2001 (02.01.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Olivia TEFY Telephone No.: (41-22) 338.83.38

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference TS 0858 PCT	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/EP 00/04997	International filing date *(day/month/year)* 30/05/2000	(Earliest) Priority Date *(day/month/year)* 03/06/1999
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**
   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
      [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
      [ ] contained in the international application in written form.
      [ ] filed together with the international application in computer readable form.
      [ ] furnished subsequently to this Authority in written form.
      [ ] furnished subsequently to this Authority in computer readble form.
      [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
      [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
2. [ ] **Certain claims were found unsearchable** (See Box I).
3. [ ] **Unity of invention is lacking** (see Box II).
4. With regard to the **title**,
   [X] the text is approved as submitted by the applicant.
   [ ] the text has been established by this Authority to read as follows:
5. With regard to the **abstract**,
   [X] the text is approved as submitted by the applicant.
   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.
6. The figure of the **drawings** to be published with the abstract is Figure No. 1
   [X] as suggested by the applicant.
   [ ] because the applicant failed to suggest a figure.
   [ ] because this figure better characterizes the invention.
   [ ] None of the figures.

PROPENE RECOVERY

The invention is directed to a process to separate propene from the product stream obtained in a fluidized catalytic cracking process.

In a fluid catalytic cracking (FCC) process a mixture of hydrocarbons is prepared by means of catalytic cracking of a petroleum distillate or residue fraction. The hydrocarbon reactor effluent is separated in a separation section into gasoline, light and heavy cycle oil and gaseous products, for example methane, LPG, propene and butene. In a conventional separation section the reactor effluent is first separated in a so-called main fractionator. The top product obtained in the main fractionator will comprise next to the so-called permanent gases like hydrogen, methane and nitrogen a certain amount of ethene, ethane, propene, propane and other saturated and unsaturated hydrocarbon compounds having a boiling point of below 220 °C. The valuable hydrocarbon compounds boiling in the gasoline range are recovered from this top product in a so-called unsaturated gas plant as described in US-A-4605493.

US-A-4605493 describes a process in which the top product of the main fractionator is first compressed in one or more stages to a higher pressure level. This section is also referred to as the recontacting section. After the recontacting section the gaseous compounds having a boiling point of ethane and below are separated from the hydrocarbon products having a boiling point of at least propene and above by means of distillate separation step. This distillate separation step comprises in that the compressed top product is separated in a gaseous fraction and a liquid fraction by means of a

flash operation. The gaseous fraction is sent to an absorber section and the liquid product is sent to a stripping section. In the combined absorber and stripping section propene, propane and higher boiling hydrocarbon compounds are separated from the gaseous compounds including ethane and ethene and lower boiling compounds. In the embodiment illustrated in US-A-4605493 the absorber and stripping sections are represented by two separate vessels. Embodiments in which both sections are present in one column are also known from the prior art.

Propene has become an important by-product of a FCC unit operation. The importance of this by-product is for example illustrated by the fact that dedicated ZSM-5 containing catalyst additives are used to enhance the propene yield in a FCC unit operation. A problem often associated with the increase in propene yield above the design value of an existing plant is that the above described rectifying absorber becomes a bottleneck. This bottleneck may for example result in that the part of the extra propene prepared in the FCC reactor will not be separated from the gaseous products in the rectifying absorber. Recovery of propene from the gaseous product downstream of the rectifying absorber is economically less attractive.

The object of the present invention is to provide a process in which propene can be separated from the gaseous FCC products with a higher efficiency than is possible with prior art processes.

This object is achieved by the following process:
Process to separate propene from gaseous fluid catalytic cracking products by performing the following steps:

a) separating a feed mixture comprising the gaseous products, propene and other saturated and unsaturated hydrocarbons obtained in a fluid catalytic cracking

process into a hydrocarbon-rich liquid fraction and a hydrogen containing gaseous fraction,

b) separating the hydrogen containing gaseous fraction into a hydrogen-rich gaseous fraction and a hydrocarbon-rich gaseous fraction by means of a membrane separation,

c) supplying the hydrocarbon-rich gaseous fraction obtained in step (b) to an absorber section and obtaining in said absorber section a lower boiling fraction rich in gaseous products having a boiling point of ethane or below and supplying the hydrocarbon-rich liquid fraction obtained in step (a) to a stripper section and obtaining in said stripper section a higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethane.

Applicants have found that by separating of part of the hydrogen present in the feed to the rectifying absorber in step (c) that the efficiency of the propene recovery is improved. This improvement enables one, for example, to either make use of smaller distillate units for new FCC units or to de-bottleneck existing FCC units enabling a higher propene production. An additional advantage is that hydrogen is obtained having a reasonable good quality in a relatively simple manner when compared to methods which can recover hydrogen from gaseous fractions at a point more down stream of the rectifying absorber. A further advantage is that in step (b) part of the sour gasses like H_2S and HCN are removed with the hydrogen, thereby reducing the amount of corrosive compounds in step (c).

The feed mixture of step (a) is a mixture obtained in a FCC main fractionator comprising gaseous products and saturated and unsaturated hydrocarbons ranging from

methane to hydrocarbons having an atmospheric boiling point of about 250 °C and preferably to about 220 °C. Apart from hydrogen the gaseous FCC products comprise various components like NH_3, H_2S, CO, CO_2, and H_2O. The feed mixture has a pressure typically between 11 and 25 bars. The content of hydrogen in the hydrogen containing gaseous fraction will suitably be 3 vol.% or higher. In a typical FCC process the hydrogen content in the hydrogen containing gaseous fraction will be between 5-20 vol.%.

The separation in a liquid and gaseous fraction in step (a) can be achieved by a conventional flash operation, for example in a knock out vessel. It has been found advantageous to reduce the contaminant level (especially NH_3 and H_2S) of the hydrogen containing gaseous fraction sent to step (b). This leads to a more hydrogen-rich gaseous fraction in step (b). Removal of sour gasses can be achieved by conventional methods. For example by contacting the feed prior to step (a) with water and separating in step (a) the feed mixture into a sour water fraction and the above mentioned hydrocarbon-rich liquid fraction and hydrogen containing gaseous fraction. Such a separation may be suitably performed in a three phase separation vessel.

Step (b) can be performed by making use of conventional membrane separation means, which are known to be selective of separating hydrogen from small hydrocarbons. Selective separation occurs when a pressure gradient across the membrane is applied. Preferably a hydrogen separation selectivity greater than 20, more preferably greater than 50, is required, wherein the selectivity is defined as the permeability ratio of hydrogen over methane. Permeability is defined as the

number of moles of a compound which permeates a membrane per square meters per day per bar of pressure difference.

It is also advantageous for the propene recovery in step (c) when membranes are used through which methane and ethane will permeate significantly faster than the heavier hydrocarbons (C_3+). Preferably the membrane has a methane separation selectivity of greater than 5, wherein the selectivity is defined as the permeability ratio of methane over propane. Suitable membranes should further have a sufficient permeation rate for the hydrogen and should have a sufficient life time. Preferred membranes further show a good resistance to liquid hydrocarbons. The membranes can be made from either inorganic or organic material. Examples of inorganic materials are ceramic, carbon and molecular sieve materials. An example of a ceramic membrane is described in US-A-5827569. Organic membrane materials are preferably of a polymer material, for example polyaramid, polyetherimide and polyimid. Examples of commercial membrane systems which can be used in the process according to the invention are Medal of L'Air Liquide, Prism alpha of Air Products, Polysep of UOP and Membrane Systems (e.g. module B-H) of Ube.

The membrane is suitably in the form of a hollow fibre placed in a membrane unit in a conventional manner known to one skilled in the art. In such a membrane unit a bundle of hollow membrane fibres are placed in a vessel in such a manner that hydrogen present in the feed to the unit can pass the membrane fibre from the shell side to the inside of the fibre resulting in a second gaseous fraction rich in hydrogen and a gaseous fraction enriched in hydrocarbons. The vessel has outlet conduits and spaces to collect the hydrogen rich gaseous fraction collected in the fibres and inlet means at the shell side

for the gaseous fraction and outlet means for the hydrocarbon rich fraction. In a preferred embodiment a number of such vessels are arranged in series in order to achieve the desired separation and to avoid the use of large vessels.

The temperature in step (b) is preferably at least 20 °C higher than the dew point of the hydrogen containing gaseous mixture send to step (b) when membrane materials are used which are sensitive to liquid hydrocarbons. Additional means for heating this gaseous mixture should then be provided to heat the hydrogen containing mixture prior to step (b). Preferably the temperature in step (b) is between 50-100 °C and more preferably between 70-90 °C.

The hydrogen containing gaseous fraction in step (b) suitably will have a pressure greater than 11 bar, preferably greater than 15 bar which enables an efficient separation in step (b). The pressure ratio of the pressure of the hydrogen containing gaseous mixture send to step (b) and the hydrogen-rich gaseous mixture obtained in step (b) is suitably greater than 2 and preferably greater than 5. Although the separation rate is negatively influenced when a low pressure ratio is used, it may in some cases be advantageous when the resulting higher pressure hydrogen-rich gaseous fraction is further purified. When the hydrogen-rich fraction is used as fuel higher pressure ratios may advantageously be applied. Preferably more than 50% of the hydrogen present in the hydrocarbon feed mixture is separated in step (b).

In step (c) the hydrocarbon-rich gaseous fraction obtained in step (b) is supplied to an absorber section. This absorber section may be a single column or a combination of more columns which comprise at least means to condense the gaseous top product, means to recycle the condensed top product to the absorber section and means

to discharge a higher boiling liquid fraction to the stripper section. This liquid fraction may be advantageously send to step (a) in order to separate any gaseous compounds in this fraction before sending it to the stripper section. This latter embodiment is illustrated in US-A-4605493.

The absorber section may further be suitably provided with means to supply a liquid hydrocarbon mixture, which mixture is poor in at least propene, to the top or discharge end of the absorber section. This hydrocarbon mixture, also referred to as lean oil, serves to absorb into the liquid phase as much propene and other valuable higher boiling hydrocarbons in the absorber section before being discharged to the stripper section. Examples of suitable sources of lean oil are the higher boiling fraction obtained in a debutanizer or the condensed fraction directly obtained from the top product of the main fractionator of a fluidized catalytic cracking process. In the condenser the lower boiling gaseous fraction rich in gaseous products having a boiling point of ethane or below is obtained.

In step (c) the hydrocarbon-rich liquid fraction obtained in step (a) is supplied to a stripper section. The stripper section is provided with reboiler means to evaporate any lower boiling compounds resulting in a gaseous fraction, means to discharge the higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethane and means to discharge the gaseous fraction to the absorber section. This gaseous fraction may be send to step (a) before being supplied to the absorber section as illustrated in US-A-4605493. However preferably the gaseous fraction obtained in the stripping section is send directly to the absorber section in order to achieve that the hydrogen concentration in the hydrogen containing gaseous fraction

obtained in step (a) is as high as possible. A higher hydrogen concentration is favourable for the efficiency of the membrane separation in step (b).

The stripper section may be a single column or a combination of more columns. An example of an embodiment of step (c) is described in the afore mentioned US-A-4605493. In a preferred embodiment absorber section and the stripping section are combined in one distillation column, optionally provided with one or more additional side-coolers and reboilers. Such a combined column is referred to as a so-called rectifying absorber.

It has been found that the propene recovery is even further improved when the hydrocarbon-rich liquid fraction obtained in step (a) is fed to a position in the rectifying absorber column above the feed inlet of the hydrocarbon rich gaseous fraction obtained in step (b). Preferably between 2-6 practical trays are present between these two inlets.

The operation conditions in the rectifying absorber may be those conventionally applied. The pressure at the top may typically range between 10 and 25 bars and the bottom temperature between 110 and 140 °C.

The higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethene obtained in step (c) can be further processed in a conventional manner in which propene is recovered by distillation from the other hydrocarbon products.

The invention shall be illustrated making use of Figure 1A and Figure 1. Figure 1A represents a rectifying absorber column according to the state of the art. Via stream (1) a feed mixture comprising gaseous products, propene and other saturated and unsaturated hydrocarbons is supplied to a knock out vessel (2) resulting in a hydrocarbon-rich liquid fraction which is discharged via stream (4) to the rectifying absorber column (5) and a

hydrogen containing gaseous fraction which is discharged via stream (3) to the rectifying absorber column (5). The rectifying absorber column (5) is equipped with a gas outlet (8) for the gaseous top fraction, a condenser (9) and a condenser collection vessel (10) in which the gaseous components are separated via (11) from the condensed liquid fraction which liquid fraction is recycled via (12) to the top of the column. Via stream (13) lean oil is mixed with the gaseous top product up-stream of condenser (9). Most of the propene present in the gaseous fraction present in stream (8) will be absorbed by the lean oil and returned to the rectifying absorber via (12). The rectifying absorber is further equipped with a reboiler (7). Via stream (6) the liquid bottom fraction enriched in propene is discharged to downstream separation units.

Figure 1 represents a process according to the invention. The meaning of the reference signs is the same as in Figure 1A. In addition to the process represented in Figure 1A a membrane separation unit (14) is shown in which a hydrogen-rich gaseous fraction is obtained and discharged via (16) and a hydrocarbon-rich gaseous fraction is obtained which is supplied to the rectifying absorber column (5) via (15).

The invention is especially directed to a method for retrofitting an existing separation unit which is part of the down stream separation means of a fluid catalytic cracking unit, and wherein in the separation unit the gaseous compounds having a boiling point of ethane and below are separated from the hydrocarbon products having a boiling point of at least propene. The existing separation unit, which has also been described above, comprises an absorber and stripping sections and separation flash means in which the hydrocarbon feed is first separated in a liquid and gaseous fraction.

Preferably the absorber and stripping sections are combined in one rectifying absorber column. The retrofitting comprising adding means to remove hydrogen, preferably by means of membrane separation, from the gaseous fraction obtained in the flash separator. Preferably use is made of existing feed inlets in the respective absorber and stripping sections for the gaseous fraction obtained in the membrane unit and the liquid fraction obtained in the flash separator.

The invention is also directed to the use of a membrane separator to remove hydrogen from a feed of a distillate separation unit which is used to separate gaseous compounds having a boiling point of ethane and below from hydrocarbon products having a boiling point of at least propene.

The invention will be illustrated by the following non limiting examples which are calculations using a mathematical model describing the knock out vessel and the rectifying absorber. A conventional value for the membrane separation efficiency is used.

Example 1

To a knock out vessel a typical FCC compressed top product of the main fractionator is sent having a pressure of 17.1 bar. Hydrogen was separated from the gaseous mixture as obtained in the knock out vessel in a membrane separation unit resulting in a gaseous mixture rich in hydrocarbons. The hydrogen rich gaseous fraction obtained has a pressure of 2 bars. The hydrocarbon-rich mixture is supplied to a typical rectifying absorber at the same feed inlet location as the feed inlet location of the liquid fraction obtained in the knock out vessel. The propene recovery is 95.1% calculated on the feed mixture. See also Table 1.

Example 2

Example 1 is repeated except that the feed inlet of the gaseous mixture rich in hydrocarbons is 4 practical trays below the feed inlet of the liquid fraction obtained in the knock out vessel. The feed inlet position of the liquid fraction is the same as used in Example 1. The propene recovery is 96.1% calculated on the feed mixture. See also Table 1.

Example 3

Example 1 is repeated except that the membrane area is half of the area used in Example 1. The propene recovery is 93.3% calculated on the feed mixture. See also Table 1.

Example 4

Example 1 is repeated except that the membrane area is 50% larger than the area used in Example 1. The propene recovery is 95.8% calculated on the feed mixture. See also Table 1.

Comparative experiment A

Example 1 is repeated except that the mixture having the composition (I) is supplied directly to the rectifying absorber without making use the knock out vessel and the membrane unit. The location of the feed inlet is the same as in Example 1. The propene recovery is 89.2% calculated on the feed mixture.

Table 1

Example→	1	2	3	4
membrane area (M^2)	6000	6000	3000	9000
Pressure of stream (11) (bar)	16.3	16.3	16.3	16.3
Fraction of H_2 removed (% on feed)	76	76	56	84
propene recovery (% on feed)	95.1	96.1	93.3	95.8
capacity increase compared to base case: Comparative experiment A	6%	11%	5%	9%

C L A I M S

1. Process to separate propene from gaseous fluid catalytic cracking products by performing the following steps:

a) separating a feed mixture comprising the gaseous products, propene and other saturated and unsaturated hydrocarbons obtained in a fluid catalytic cracking process into a hydrocarbon-rich liquid fraction and a hydrogen containing gaseous fraction,

b) separating the hydrogen containing gaseous fraction into a hydrogen-rich gaseous fraction and a hydrocarbon-rich gaseous fraction by means of a membrane separation,

c) supplying the hydrocarbon-rich gaseous fraction obtained in step (b) to an absorber section and obtaining in said absorber section a lower boiling fraction rich in gaseous products having a boiling point of ethane or below and supplying the hydrocarbon-rich liquid fraction obtained in step (a) to a stripper section and obtaining in said stripper section a higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethane.

2. Process according to claim 1, wherein to the top or discharge end of the absorber section a liquid hydrocarbon mixture is supplied to, which hydrocarbon mixture is poor in propene.

3. Process according to any one of claims 1-2, wherein the gaseous fraction obtained in the stripping section is supplied directly to the absorber section.

4. Process according to any one of claims 1-3, wherein the higher boiling liquid fraction obtained in the absorber section is supplied to step (a).

5. Process according to any one of claims 1-2, wherein the stripping section and the absorber section are combined in one distillation column.

6. Process according to claim 5, wherein the hydrocarbon rich liquid fraction obtained in step (a) is fed to a position in the distillation column above the feed inlet of the hydrocarbon rich gaseous fraction obtained in step (b).

7. Process according to any one of claims 1-6, wherein the hydrogen separation selectivity of the membrane separation in step (b) is greater than 20, wherein the hydrogen separation selectivity is defined as the permeability ratio of hydrogen over methane.

8. Process according to any one of claims 1-7, wherein the methane separation selectivity of the membrane separation in step (b) is greater than 5, wherein the methane separation selectivity is defined as the permeability ratio of methane over propane.

9. Method for retrofitting an existing separation unit for separating a feed into a gaseous fraction comprising compounds having a boiling point of ethane and below and a liquid fraction comprising hydrocarbon products having a boiling point of at least propene, which separation unit comprises an absorber and stripping sections and separation flash means in which the feed is first separated in a liquid and gaseous fraction and means to supply the gaseous fraction to the absorber section and means to supply the liquid fraction to the stripping section, wherein the retrofitting comprises adding membrane separation means which remove part of the hydrogen from the gaseous fraction before supplying said gaseous fraction to the absorber section.

10. Use of a membrane separator to remove hydrogen from a feed of a distillate separation unit which is used to separate gaseous compounds having a boiling point of

ethane and below from hydrocarbon products having a boiling point of at least propene.

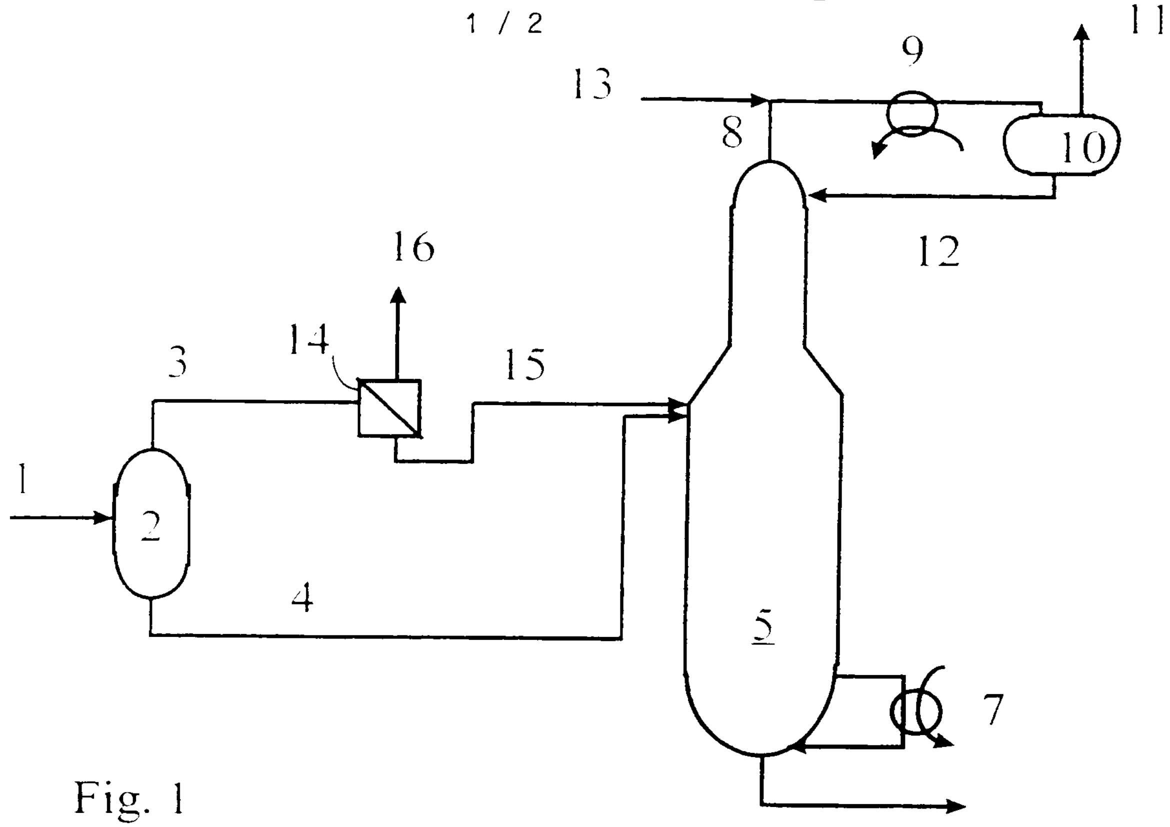

Fig. 1

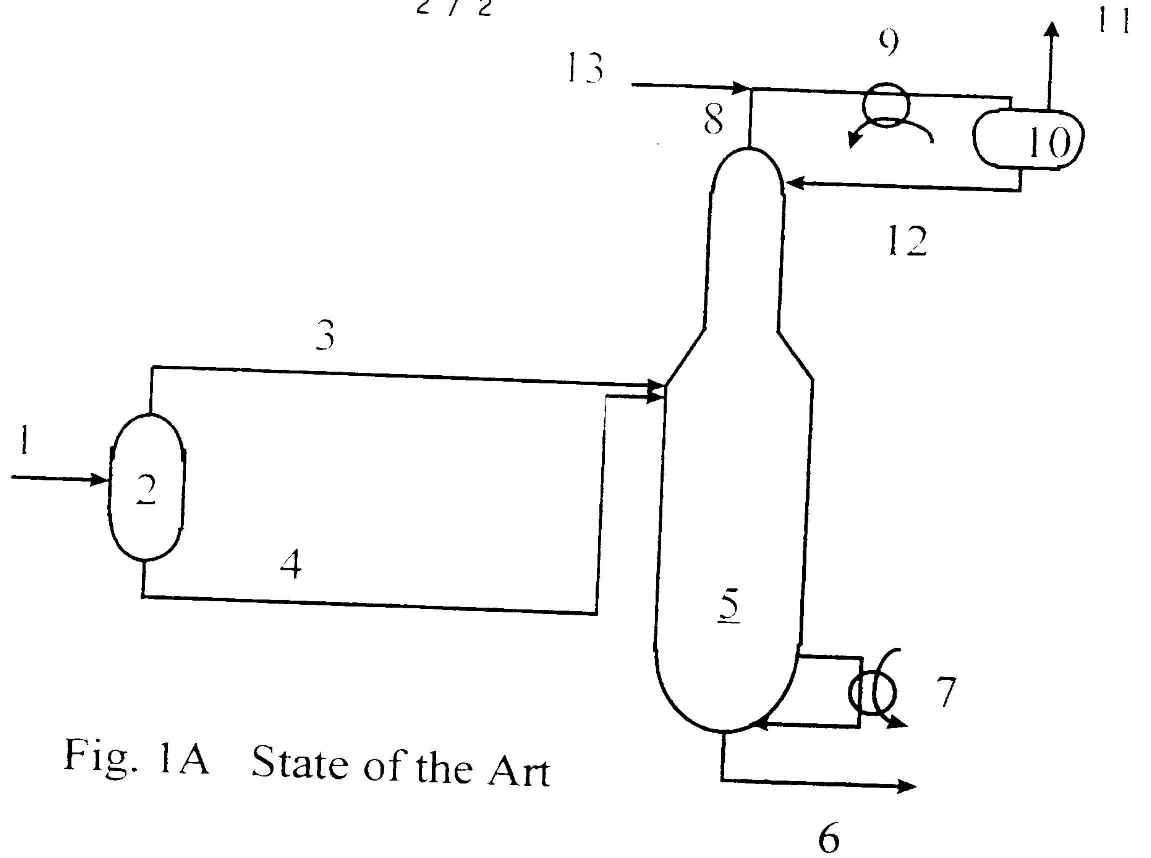

Fig. 1A State of the Art

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/04997

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G70/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 605 493 A (HARANDI MOHSEN N) 12 August 1986 (1986-08-12) cited in the application the whole document	1-10
Y	US 5 452 581 A (DINH CONG X ET AL) 26 September 1995 (1995-09-26) the whole document	1-10
A	US 5 634 354 A (HOWARD LEE J ET AL) 3 June 1997 (1997-06-03) the whole document	1-10

[ ] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 September 2000	26/09/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Michiels, P

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 00/04997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4605493 A	12-08-1986	AU 584147 B	18-05-1989
		AU 5116185 A	10-07-1986
		CA 1254165 A	16-05-1989
		DE 3582050 D	11-04-1991
		EP 0188124 A	23-07-1986
		JP 7015100 B	22-02-1995
		JP 61162588 A	23-07-1986
		JP 63291984 A	29-11-1988
		US 4714524 A	22-12-1987
US 5452581 A	26-09-1995	CA 2145014 A	02-10-1995
US 5634354 A	03-06-1997	BR 9701965 A	15-09-1998
		EP 0806468 A	12-11-1997
		JP 2977127 B	10-11-1999
		JP 10053774 A	24-02-1998
		KR 210529 B	15-07-1999
		SG 45544 A	16-01-1998

CLAIMS

1. Process to separate propene from gaseous fluid catalytic cracking products by performing the following steps:

a) separating a feed mixture comprising the gaseous products, propene and other saturated and unsaturated hydrocarbons obtained in a fluid catalytic cracking process into a hydrocarbon-rich liquid fraction and a hydrogen containing gaseous fraction,

b) separating the hydrogen containing gaseous fraction into a hydrogen-rich gaseous fraction and a hydrocarbon-rich gaseous fraction by means of a membrane separation,

c) supplying the hydrocarbon-rich gaseous fraction obtained in step (b) to an absorber section and obtaining in said absorber section a lower boiling fraction rich in gaseous products having a boiling point of ethane or below and supplying the hydrocarbon-rich liquid fraction obtained in step (a) to a stripper section and obtaining in said stripper section a higher boiling fraction comprising propene and hydrocarbons having a boiling point higher than ethane.

2. Process according to claim 1, wherein to the top or discharge end of the absorber section a liquid hydrocarbon mixture is supplied to, which hydrocarbon mixture is poor in propene.

3. Process according to any one of claims 1-2, wherein the gaseous fraction obtained in the stripping section is supplied directly to the absorber section.

4. Process according to any one of claims 1-3, wherein the higher boiling liquid fraction obtained in the absorber section is supplied to step (a).

5. Process according to any one of claims 1-2, wherein the stripping section and the absorber section are combined in one distillation column.

6. Process according to claim 5, wherein the hydrocarbon rich liquid fraction obtained in step (a) is fed to a position in the distillation column above the feed inlet of the hydrocarbon rich gaseous fraction obtained in step (b).

7. Process according to any one of claims 1-6, wherein the hydrogen separation selectivity of the membrane separation in step (b) is greater than 20, wherein the hydrogen separation selectivity is defined as the permeability ratio of hydrogen over methane.

8. Process according to any one of claims 1-7, wherein the methane separation selectivity of the membrane separation in step (b) is greater than 5, wherein the methane separation selectivity is defined as the permeability ratio of methane over propane.

9. Method for retrofitting an existing separation unit for separating a feed into a gaseous fraction comprising compounds having a boiling point of ethane and below and a liquid fraction comprising hydrocarbon products having a boiling point of at least propene, which separation unit comprises an absorber and stripping sections and separation flash means in which the feed is first separated in a liquid and gaseous fraction and means to supply the gaseous fraction to the absorber section and means to supply the liquid fraction to the stripping section, wherein the retrofitting comprises adding membrane separation means which remove part of the hydrogen from the gaseous fraction before supplying said gaseous fraction to the absorber section.

10. Use of a membrane separator to remove hydrogen from a feed of a distillate separation unit which is used to separate gaseous compounds having a boiling point of

ethane and below from hydrocarbon products having a boiling point of at least propene.

PATENT COOPERATION TREATY

PCT

REC'D 13 AUG 2001
WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference TS 0858 PCT	**FOR FURTHER ACTION** See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP00/04997	International filing date *(day/month/year)* 30/05/2000	Priority date *(day/month/year)* 03/06/1999
International Patent Classification (IPC) or national classification and IPC C10G70/04		
Applicant SHELL INTERNATIONALE RESEARCH ... et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand 02/01/2001	Date of completion of this report 09.08.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Falls, F Telephone No. +49 89 2399 8350

Form PCT/IPEA/409 (cover sheet) (January 1994)

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, pages:

1-11	as originally filed

Claims, No.:

1-7	as received on	29/05/2001	with letter of	29/05/2001

Drawings, sheets:

1/2,2/2	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-7
	No:	Claims	
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-7
Industrial applicability (IA)	Yes:	Claims	1-7
	No:	Claims	

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

I

1). Prior Art

It is considered that **US-A5452581(D1)** contains the most relevant prior art. It discloses the separation of an olefin-containing feed into a hydrogen-rich gas fraction and a liquid fraction and then separation of the gas stream into H_2 and HC-rich streams using a membrane (see Cl. 1).

It is considered that **US-A-4605493(D2)** is less relevant than D1 because it only discloses absorber and stripper sections but not a membrane separator.

2). Novelty (Art. 33(2) PCT)

The following interpretation of part (c) of claim 1 is given: The term "absorber section" as used in the application refers to anything which results in condensation of part of the gaseous phase and the term "stripper section" to anything which results in removal of vapour from the liquid phase (see description, bridging paragraphs pages 6-7 and 7-8 respectively). Moreover in a significant embodiment of claim 1 the 2 processes of absorption and stripping can occur at the same locaton within the system (e.g. see example 1, pg 10).

In view of these considerations both features of part (c), i.e. processing of the HC-rich gas fraction from (b) in an "absorber" section and processing of the HC-rich liquid fraction from (a) in a "stripper" section to obtain fractions as described in (c) are disclosed by D1 to condense an olefin phase from the hydrogen-lean stream and direct the condensate to a vapor-liquid separator (see Cl. 2 and Fig 1 & supporting passage in col. 7, l. 35-52).

It is noted that while claim 1 refers to "a process to separate propene from gaseous FCC products" there are no actual steps of separation and recovery of propene; rather the products of the process as in part (c) would be a condensed phase from the HC-rich gas fraction which may contain a substantial amount of propene and a liquid fraction from stripping of the HC-rich liquid fraction from (a) which would contain propene. It is considered that because of the conditions described in D1 (e.g. see col. 7, l. 35-37) the liquid fraction would certainly contain propene.

The feature "wherein to the top or discharge end of the absorber section a liquid HC mixture is supplied to, which HC mixture is poor in propene", which has been introduced by amendment into the claim, is considered so unclear (see section II below) that it cannot be considered to distinguish the subject-matter of claim 1 from the prior art.

In view of this D1 is considered to disclose the features of (a)-(c) of claim 1 except that the feed derives from FCC, the feed mixture comprises products ranging to HCs having a boiling point of 250°C and that membrane separation occurs at between 50 and 100°C. Therefore the subject-matter of claim 1 is novel (Art. 33(2) PCT).

3). Inventive Step (Art. 33(3) PCT)

However, none of the said features introduce an inventive step. One skilled in the art would certainly apply the separation process taught in D1 to an FCC product. One skilled in the art would apply the process to a feed mixture as defined in part (a); this appears to be a conventional feed mixture for recovery of light olefins. One skilled in the art would choose the parameter value of membrane temperature without the exercise of inventive skill.

It is further considered that D1 suggests the process taught as offering a solution to the problem addressed by the application (see col. 8, l. 48-53). In particular one skilled in the art would read the general teaching of D1 as a means to obtain fracions of lighter olefins other than ethene, such as propene.

The arguments offered by the applicant for not considering D1 are not accepted. The reference to a steam cracker is a single reference to the prior art in the opening part of the document. It does not limit the teaching of D1 as a whole. The other references to D1 in the letter of reply are to preferred teachings which are not directed towards propene recovery. However the relevance of D1 is that it would read by a skilled person as offering a way to recover light olefins generally.

It is not apparent that any of the features of claims 2-4 or 7 would introduce an inventive step when combined with the features of claim 1.

No arguments have been offered by the applicant that the features of claims 5 or 6 would introduce an inventive step when combined with the features of claim 1.

II

The feature "wherein to the top or discharge end of the absorber section a liquid HC mixture is supplied to, which HC mixture is poor in propene" in claim 1 is unclear (Art. 6 PCT). It fails to define the location to which the HC mixture is supplied and to define the propene content.

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The application also fails to meet the requirements of the PCT convention in the following matters:

1). The description has not been brought into conformity with the claims as required by Rule 5.1(a)(iii) PCT.

2). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the document D1 is not mentioned in the description, nor is this document identified therein.